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Note

ON THE THERMAL STABILITY OF SOME COORDINATION COMPOUNDS GENERATING MIXED OXIDES WITH PEROVSKITIC STRUCTURE. III

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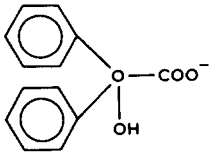
Two previous notes were dedicated to the thermal stability of some coordination compounds of rare earth metals as well as to their non-isothermal kinetic parameters [1,2]. This note deals with some new results concerning some polynuclear coordination compounds of the pairs Ln–Ni (Ln–rare earth metal) with the benzylic acid anion.

EXPERIMENTAL

Powders of the following compounds (**A**–**E**) were used:
A $[\mathrm{DyNi\,(Bz.ac)_5}]\cdot 5H_2O$
B $[\mathrm{HoNi\,(Bz.ac)_5}]\cdot 6H_2O$
C $[\mathrm{SmNi\,(Bz.ac)_5}]\cdot 7H_2O$
D $[\mathrm{NdNi\,(Bz.ac)_5}]\cdot 4H_2O$
E $[\mathrm{Nd_2Ni\,(Bz.ac)_8}]\cdot 9H_2O$
where Bz.ac is the benzylic acid anion, i.e.,



The compounds **A**–**E** were synthesized and analysed according to the methods described elsewhere [3]. The crystalline state of the solid com-

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pounds was investigated with a Philips (P.W. 1400) X-ray diffractometer using chromium K_α radiation. The heating curves between 20–1000°C were recorded with a Paulik–Paulik–Erdey type derivatograph (Q-1500 D) at heating rates between 1.25 and 10 K min^{-1} in a static air atmosphere.

The values of the non-isothermal kinetic parameters were obtained by the method of Coats and Redfern [4]. The data were processed automatically using a P.C.–Sharp–1251 and a program written in BASIC [5].

RESULTS AND DISCUSSION

The Bragg angles, θ, and interplanar distances, d, for the most intense peaks of the diffractograms as well as the crystal sizes, l, calculated accoridng to Scherrer's formula [6] are summarized in Table 1.

The X-ray diffractograms of the decomposition products at 1000°C show the presence of both Ln_2O_3 and NiO.

Some data concerning thermal stability of compounds **A**–**E** obtained from the derivatograms are given in Table 2.

For the compounds investigated, partial thermal decomposition reactions applicable to obtaining the non-isothermal kinetic parameters were: dehydration (two steps) and a decomposition step following dehydration which was relatively difficult to characterize stoichiometrically, referred to as "kinetically applicable reaction". As far as decompositions which occur at temperatures higher than 350°C are concerned, these are overlapping reactions which are difficult (if not impossible) to characterize stoichiometrically as well as kinetically. The total weight loss corresponds to the decomposition of the parent compounds into the mixture of Ln_2O_3 and NiO, thus confirming the X-ray diffraction data.

The values of the non-isothermal kinetic parameters for the "reaction order" model, namely reaction order, n, activation energy, E, and pre-exponential factor, A, are listed in Table 3.

Inspection of Table 3 shows that most of the decompositions are characterized by values of the reaction order which are equal to unity. There are only few reactions ((XII) and even (I) and (VIII)) for which the values of

TABLE 1

X-ray diffraction data

Compound	**A**	**B**	**C**	**D**	**E**
θ	11°24′	11°18′	12°31′	11°12′	11°42′
d(Å)	5.78	5.83	5.27	5.88	5.76
l(Å)	50	48	111	97	75

TABLE 2

Weight loss, temperature intervals and corresponding stoichiometric equations of solid–gas decompositions for compounds **A**–**E**

Compound	Weight loss %	Temperature Interval (°C)	Reaction[a]	
A	0.87	20–85	$[DyNi(Bz.ac)\cdot 5H_2O_{(s)} \xrightarrow{70^{\circ}C} [DyNi(Bz.ac)_5]\cdot 3H_2O_{(s)} + 2H_2O(g)$	(I)
	5.70	90–140	$[DyNi(Bz.ac)_5]\cdot 3H_2O_{(s)} \xrightarrow{130^{\circ}C} [DyNi(Bz.ac)_5]_{(s)} + 3H_2O_{(g)}$	(II)
	38.64	150–330	Kinetically applicable reaction	(III)
B	1.74	20–80	$[HoNi(Bz.ac)_5]\cdot 6H_2O_{(s)} \xrightarrow{50^{\circ}C} [HoNi(Bz.ac)_5]\cdot 4H_2O_{(s)} + 2H_2O_{(g)}$	(IV)
	6.55	85–140	$[HoNi(Bz.ac)_5]\cdot 4H_2O_{(s)} \xrightarrow{120^{\circ}C} [HoNi(Bz.ac)_5]_{(s)}\cdot 4H_2O_{(g)}$	
	62.22	145–340	Kinetically applicable reaction	(VI)
C	5.31	20–90	$[SmNi(Bz.ac)_5]\cdot 7H_2O_{(s)} \xrightarrow{70^{\circ}C} [SmNi(Bz.ac)_5]\cdot 3H_2O_{(s)} + 4H_2O_{(g)}$	(VII)
	8.99	95–140	$[SmNi(Bz.ac)_5]\cdot 3H_2O_{(s)} \xrightarrow{120^{\circ}C} [SmNi(Bz.ac)_5]_{(s)} + 3H_2O_{(g)}$	(VIII)
	31.58	150–270	Kinetically	(IX)
	71.24	270–330	applicable reactions	(X)
D	3.40	20–90	$[NdNi(Bz.ac)_5]\cdot 4H_2O_{(s)} \xrightarrow{65^{\circ}C} [NdNi(Bz.ac)_5]\cdot 3H_2O_{(s)} + H_2O_{(g)}$	(XI)
	7.65	95–120	$[NdNi(Bz.ac)_5]\cdot 3H_2O_{(s)} \xrightarrow{110^{\circ}C} [NdNi(Bz.ac)_5]_{(s)} + 3H_2O_{(g)}$	
	29.77	120–280	Kinetically applicable reaction	(XIII)
E	1.53	20– 90	$[NdNi(Bz.ac)_8]\cdot 9H_2O_{(s)} \xrightarrow{70^{\circ}C} [NdNi(Bz.ac)_8\cdot 7H_2O_{(s)} + 2H_2O_{(g)}$	(XIV)
	7.28	90–150	$[NdNi(Bz.ac)_8]\cdot 7H_2O_{(s)} \xrightarrow{130^{\circ}C} [NdNi(Bz.ac)_8]_{(s)} + 7H_2O_{(g)}$	(XV)
	24.53	160–250	Kinetically applicable reaction	(XVI)

[a] The temperatures above the arrows correspond to the maximum decomposition rates.

the pre-exponential factors correspond to those predicted by the transition state theory [7]. Thus for the other reactions to value $n = 1$ is apparent, the thermolysis being described by a particular case of J.M.A.Y.K. equation, corresponding to instantaneous nucleation followed by unidimensional

TABLE 3

Values of non-isothermal kinetic parameters of the thermal decompositions of compounds **A–E**

Compound	Heating rate (K min^{-1})	Reaction	n	E (kcal mol^{-1})	A (s^{-1})	Correlation coefficient
A	5.7	(I)	1	20.3	4.9×10^{10}	0.991
		(II)	0.8	16.8	1.5×10^{6}	0.996
		(III)	1	17.4	1.3×10^{4}	0.996
B	5.1	(IV)	1	16.5	3.5×10^{8}	0.998
		(V)	1	16.5	4.4×10^{6}	0.993
		(VI)	0.8	16.2	3.1×10^{3}	0.993
C	5.6	(VII)	1	15.3	1.1×10^{7}	0.990
		(VIII)	1	32.1	2.9×10^{15}	0.988
		(IX)	0	20.9	6.2×10^{5}	0.993
		(X)	1	53.0	9.9×10^{17}	0.988
D	3.2	(XI)	1.2	19.5	2.27×10^{10}	0.991
		(XII)	1	26.9	4.8×10^{12}	0.987
		(XIII)	0	14.8	3.8×10^{2}	0.985
E	5.7	(XIV)	1	10.7	1.8×10^{4}	0.999
		(XV)	0.8	16.7	1.6×10^{5}	0.982
		(XVI)	1.4	12.9	1.0×10^{2}	0.982

growth of nuclei [8]. In such conditions the experimental activation energy corresponds to the activation energy of the growth of nuclei.

CONCLUSIONS

The non-isothermal kinetic parameters for the thermal decomposition of five polynuclear coordination compounds of some rare earth metals with the benzylic anion have been determined.

The results obtained suggest a nucleation–nuclei growth model described by the J.M.A.Y.K. Equation.

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